PREPARATION AND CHARACTERIZATION OF POLYMER ELECTROLYTE

Thesis submitted for the Award of degree of

Master of Science

by

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Under the Academic Autonomy

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Under the Guidance of

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DECLARATION

I hereby declare that the work carried out in this thesis is entirely original. It was carried out at Department of Physics, National Institute of Technology, Rourkela. I further declare that it has not formed the basis for the award of any degree, diploma, or similar title of any university or institution.

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CERTIFICATE

This is to certify that the thesis entitled "**Preparation and Characterization of Polymer Electrolytes**" being submitted by **Smita Mahapatra** in partial fulfillment of the requirements for the award of the degree of Master of Science in Physics at National Institute of Technology, Rourkela is an authentic experimental work carried out by her under our supervision. To the best of our knowledge, the experimental matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

Date:

(Dr. Dillip Kumar Pradhan) (Dr. Sidhartha Jena)

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I express my gratitude to my parents and my sister without the help of whom the present work would not have been a success.

DEDICATED TO MY

PARENTS

ABSTRACT

Two group of polymer electrolytes having Na^+ ion as the principal charge carrier have been prepared and analyzed with different experimental techniques. In the present study, sodium perchlorate ($NaClO_4$) was taken as the salt and two different polymers (i.e. Polyethylene Oxide (CH_2 -CH_2-O) and Polyurethane (RNHCOOR′)) were taken as polymer host for polymer-salt complexation. The polymer electrolytes were prepared by the solution cast method having different O/Na ratio (O/Na = 0, 4, 8, 20, 40, 60, 80, 100). The structural and morphological characterization was carried out using X-ray diffraction (XRD) and Scanning electron microscopy (SEM) analysis. XRD analysis showed the formation of polymer-salt complexation with the existence of both crystalline and amorphous phases in the materials. Again the formation of salt-polymer complexation has been confirmed by FTIR analysis by observing the COC stretching modes. The electrical property of the polymer electrolytes were carried out using complex impedance analysis in the frequency range of 100 mHz to 1 MHz at room temperature. AC conductivity, dielectric property and impedance data were presented with respect to different frequency and different compositions.

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CHAPTER-1

INTRODUCTION

"Solid-state Ionics "is the branch of science and technology which deals with the study of materials and applications aspect of ionically conducting solids. All types of electrolytes come under the branch of solid state Ionics.

1.1 ELECTROLYTE:

A substance that conducts electricity through the movement of ions is known as electrolyte. Most of the people have general idea that electrolyte is an ionic solution i.e., liquid electrolyte.

LIQUID ELECTROLYTE:

Liquid electrolytes are normally formed when a salt is dissolved into a solvent such as water or any other polar solvents the individual components dissociate due to the thermodynamic interactions between the solvent and the solute molecules**.** For example:-$\mathbf{NaCl_{(s)} \rightarrow Na^{+}_{(aq)} + Cl^{-}.}$ When NaCl is dissolved in water it dissociates into $Na^{+}$and Cl^{-}due to the interaction between solvent and solute molecule which form the liquid electrolyte. Liquid electrolyte is mainly used in electrochemical devices. Most of the electrochemical devices have mainly three components i.e., (i) cathode, (ii) anode and (iii) electrolyte as shown in Figure. 1.

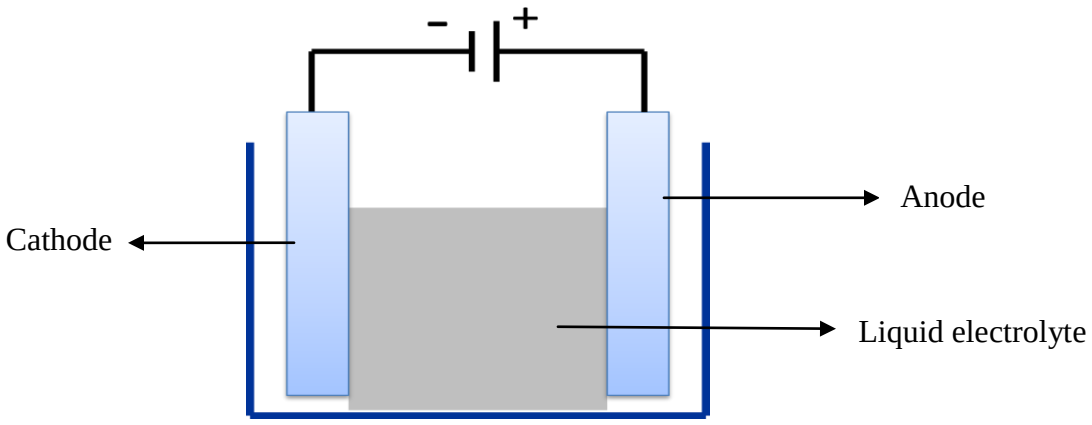


Fig 1.1A Typical Electrochemical Device

DISADVANTAGES OF LIQUID ELECTROLYTES:

There are quite a few disadvantages of the liquid electrolytes being used in these devices. The immediate consequence of the liquid electrolytes is leakage and can be hardly controlled owing to the flow of the liquids. Further the electrolytic solution used tends to corrode the electrodes thus rendering the device useless. The solvent used limits the temperature range of operation of these devices. They have low energy density. Apart from these drawbacks the devices using liquid electrolytes are bulky and difficult to be transported or carried. Presently when we are striving for the miniaturization of the devices, the liquid electrolytes only adds to our troubles. The advent of the solid electrolytes has not only eliminated the above mentioned problems but also provides more flexibility. Moreover with the solid electrolytes at our disposal the miniaturization of devices is no longer an idea but has been transformed into reality. The following section gives a brief discussion of the solid electrolytes, their properties and applications.

1.2. SOLID ELECTROLYTES/FAST ION CONDUCTOR/SUPERIONIC SOLID:

A solid electrolyte should have the following characteristics

I. Ionic conductivity should be very high (i.e., 10^{-1}-10^{-4} Scm^{-1}) at room temperature with negligible electronic conduction ($<10^{-6}$ Scm^{-1}).
II. In solid electrolyte ions should be principal charge carrier i.e., ionic transference should be close to unity (t_{ion}~ 1).
III. Activation energy should be very low.

Applications of Ionic Conductors-

- Batteries
- Fuel Cells
- Gas Sensors
- display devices

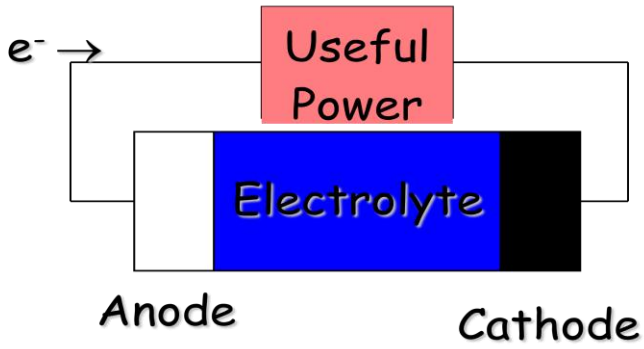


Fig 1.2 Solid Electrolytic cell [1,2]

1.3 CLASSIFICATION OF IONIC CONDUCTORS:

The solid electrolytes can be classified into four types, depending on their microstructure and physical properties [3].

- Framework crystalline/ polycrystalline materials
- Composite or dispersed phase electrolytes
- Amorphous glassy electrolytes
- Polymer electrolytes

Solid polymer electrolytes (SPEs) have the advantages over other solid electrolytes of desirable shape mouldability, mechanical strength, higher safety due the absence of flammable organic solvent and flexibility of design thereby permitting miniaturization. Polymeric materials have better mechanical properties for the construction of all practical solid-state electrochemical cells.

The discussion on polymer electrolyte is the scope of this thesis.

1.4 POLYMER ELECTROLYTE:

To prepare polymer electrolytes, generally polymers are taken as host material. Polymers are generally electrical insulators and their properties (thermal, electrical and mechanical) can be modified by complexation with a salt and dispersal of a second phase. Polymer electrolytes are usually formed from thermoplastic elastomers. For the preparation of polymer-electrolyte (i.e., polymer-salt complex), following guidelines should be adopted while choosing the polymer and the salt

I. Polymer that forms complexation with salt should have polar group (Lewis bases) on the polymer chain.
II. Polymer should have high molecular weight and low glass transition temperature.
III. The salts having low lattice energy are most likely to form polymer salt complexation. These salts usually contain univalent alkali ions with larger anions (e.g.,$CF_3SO_3^-$,I^- , ClO_4^- , HPO_4^- etc).
IV. Polymers with low cohesive energy density and high flexibility have the greatest tendency to interact with salts.

Due to their high molecular weight, they exhibit macroscopic properties that behave like a true solid at an atomic level. Local relaxation provides liquid like degrees of freedom that are not significantly different from those of conventional liquid. Also polymers are not brittle, so that they are able to form good interfacial contacts with electrode materials.

Due to the above excellent properties of the polymers, the idea of using polymer electrolyte has been conceived by the scientific community as compared to other solid electrolytes. In the present study we have chosen Polyethylene Oxide (CH_2 -CH_2-O) and Polyurethane (RNHCOOR′) as polymer host.

1.5. STRUCTURE AND MORPHOLOGY OF POLYEHYLENE OXIDE:

Polyethylene oxide (PEO) is one of the most studied polymer host for polymer electrolyte formation. It is a semi crystalline material (about 70-85% crystallinity) at room temperature and they remain present in an amorphous elastomeric phase. The partial crystallinity carries over to many of the polymer-salt complexation. Thus the problem of structure of the polymer electrolytes arises at two levels: one is the macroscopic identity due to arrangement of crystalline and amorphous phases and the other is microscopic arrangement of atoms in the polymer and polymer-salt complex. For both PEO and PEO complexes the morphology of the crystalline phases can be observed with an optical microscope. The polycrystalline phase is often crystalline in structure with well separated amorphous boundary. The ethylene oxide monomer is nothing more than an epoxide ring. Two corners of the molecule consist of -CH_2- linkages. The third corner is oxygen, -O-. The monomer forms a chain having the repeat unit of -CH_2-CH_2-O-.

It allows a high degree of crystallinity involving ~70-80%of the polymer (lamellae arranged as spehrulite). The melting point, T_m of the crystalline phase is 65°C and the glass transition temperature, Tg of the amorphous phase is - 60°C. The low dielectric constant of the polymer (~5 - 8) has a significant influence on the properties of the electrolyte and having a good structural integrity.

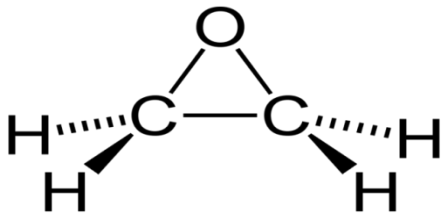


Fig 1.4Structure of the monomer of poly ethylene oxide [4]

1.6 STUCTURE AND MORPHOLOGY OF POLYURETHANE OXIDE-(C_{25} $H_{42}N_2O_6$):

Polyurethane is a polymer consisting of chains of organic units joined by urethane links. Polyurethane polymers are formed through step-growth polymerization by reacting with monomer containing at least two isocyanate functional groups with another monomer containing at least two hydroxyl (alcohol) groups in the presence of a catalyst. It is a unique material that offers the elasticity of rubber combined with the toughness and durability of metal. Because urethane is available in a very broad hardness range (eraser-soft to bowling-ball-hard), it can replace rubber, plastic and metal with the ultimate in abrasion resistance and physical properties. Polyurethane have excellent electrical insulating properties and are generally used successfully in many molded wire and cable harness assembly.

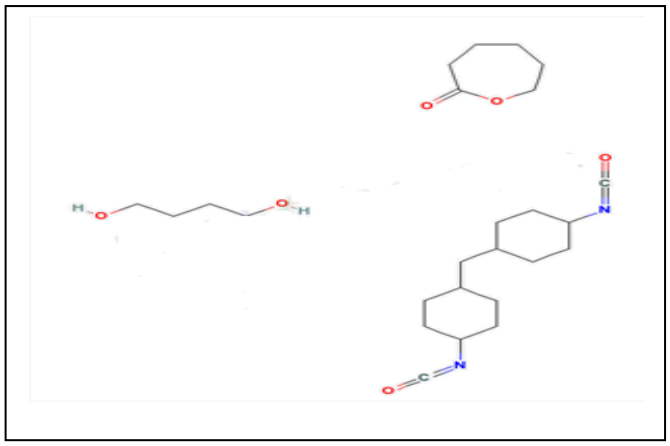


Fig1.5 structure of polyurethane

1.7 LITERATURESURVEY:

The research work on polymer electrolyte dates back to the pioneering work of Wright and co-worker, who first reported the ionic conduction in poly–ethylene oxide (PEO) and alkali metal salt complexation [5,6]. Later Armand et. al. [7] explored the potential applications of these materials for device applications. Since then lots of research activity have been carried out around the globe to find out a suitable polymer electrolyte for device applications. Till now, low ionic conductivity at ambient temperature of polymer electrolytes act as a barrier to their utility for device applications, when compared to the existing conventional liquid/hybrid electrolytes. Polymer electrolytes consisting of PEO and $LiCF_3SO_3$ were synthesized by solution cast technique for different EO/Li ratio. Dielectric spectroscopic studies were performed to understand the ion transport process in polymer electrolyte. The dielectric loss spectra showed the presence of one relaxation for all composition, which is associated with the motion of the Li-ion coordinated polymer segments [8]. Polymer electrolyte membranes consisting of a novel hyper branched polyether PHEMO (poly(3-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}methyl-3′-methyloxetane)), PVDF-HFP (poly(vinylidene fluoride-hexafluoropropylene)) and LiTFSI have been prepared by solution casting technique. The effects of different amounts of PVDF-HFP and lithium salts on the conductivity of the polymer electrolytes were studied. The ionic conductivity of the prepared polymer electrolytes were found to be $1.64 \times 10^{-4}\ S \cdot cm^{-1}$ at 30 °C and $1.75 \times 10^{-3}\ S \cdot cm^{-1}$ at 80 °C [9]. A sodium ion-conducting polymer electrolyte based on polyvinyl pyrrolidone (PVP) complexed with $NaClO_4$ was prepared using the solution-cast technique. Investigations were conducted using X-ray diffractometry (XRD), Fourier transformation infrared (FT-IR) spectroscopy. The ionic conductivity and transference number measurements were performed to characterize the polymer electrolyte for battery applications [10]. Plasticized composite polymer electrolyte based on polymer salt complex as PEO-$NaClO_4$, ceramic filler as SnO_2 and plasticizer as polyethylene glycol (PEG200) were prepared and analyzed. The effect of plasticizer concentration on changes in structural, microstructural, thermal and electrical properties has been studied. The suppression of crystallinity was observed from DSC and X ray analysis. Also an improvement in electrical conductivity has been observed without any sharp deterioration in the thermal, electrochemical or mechanical stability of the

PCPE thin films [11]. Blend-based polymer electrolytes of poly(ethylene oxide) (PEO) and fully amorphous cross-linked poly(ethylene oxide-co-propylene oxide) (poly(EO/PO)) were prepared and their thermal behavior, surface morphology, electrical and mechanical properties were systematically investigated. Experimental results showed the crystallization tendency of PEO in the blend-based polymer electrolytes. It showed excellent mechanical strength [12].

1.8 MAIN OBJECTIVE:

The following are the main objective of the present work

I. Synthesis of polymer electrolyte by solution cast technique.
II. Structural characterization of polymer electrolytes by X-ray diffraction technique.
III. Vibrational characterization using FTIR technique
IV. Micro structural characterization using Scanning Electron Microscopy (SEM)
V. Studies of frequency dependence of dielectric and ac electrical conductivity for better understanding of ion transport mechanism in polymer electrolyte.

Materials under present investigation:

Group1- $(PEO)_x$-$NaClO_4$ (x=0,4,8,20,40,60,80,100)

Group 2- PU_x-$NaClO_4$ (x=0, 4, 8, 20, 40, 60, 80,100)

1.9 ORGANIZATION OF THE THESIS –The thesis consists of four chapters.

CHAPTER1: This chapter gives an idea about solid state Ionics, liquid electrolyte, solid polymer electrolyte and structure of PEO and PU. In addition to that the past work done on the polymer electrolyte and main objective of the work is briefly described.

CHAPTER2: The different methods of preparation of polymer electrolyte and the adopted procedure are discussed along with different characterization techniques.

CPAPTER3- This chapter deals with the structural, micro structural and vibrational characterization carried out by XRD, SEM and IR spectroscopy. It also gives detailed studied of the electrical property of polymer electrolyte with the help of impedance spectroscopy analysis at different frequency. Resistance is being calculated from the complex impedance plot.

CHAPTER 4- Summary and conclusion of the present work is being given.

CHAPTER-2

2. SAMPLE SYNTHESIS

2.1 DIFFERENT METHOD OF PREPARATION:

There are different methods of preparation of polymer electrolytes. Below we are discussing some methods of preparations.

Casting Method: It is a simple and frequently used method. It can produce polymer film of varying thickness ranging from several micrometers up to several millimeters. Generally, this method includes the following steps: (a) polymer dissolved in the solvent and allowed to be swollen, (b) Addition of a specified amount of salt to the polymer solutions, (c) Mixing by means of stirrer or ultrasonic equipment for complexatation, (d) Addition of a specified amount of filler/plasticizer to the polymer solutions, (e) Casting the mixture on a glass plate/petridish/substrate (e) Finally drying in vacuum or in an atmosphere of argon.

Spin Coating: The spin-coating method is very similar to the casting method. Instead of casting the film on a substrate, in this method, the mixture is dropped on a substrate and placed in a spin coater that can be rotated at an adjustable rotation speed. The film thickness can be controlled easily by adjusting the viscosity (concentration) of the mixture and the speed of the rotation. However, this method is only available if the viscosity of the mixture is not too high. For a gel mixture, the spin coater rotation is not enough to spread the mixture droplet to form thin film.

Hot Press: The hot press equipment consists of: (A) weighing cylinder, (B) heating chamber, (C) basement, and (T) temperature controller as shown in the Figure 2.1. Suitable amounts of polymer, salt, and filler are mixed in a mortar for about several minutes. The powder mixture is then sandwiched between two sheets of Mylar or other materials, and positioned inside the heating chamber. The heating chamber is controlled at temperatures slightly above the melting point of the polymer. If PEO is used as polymer matrix, temperature of 80^0C is suitable. The sample is then pressed by applying pressure. The weighing cylinder can controlled the pressure. After heating and pressing, the sample is then slowly cooled to room temperature [13].

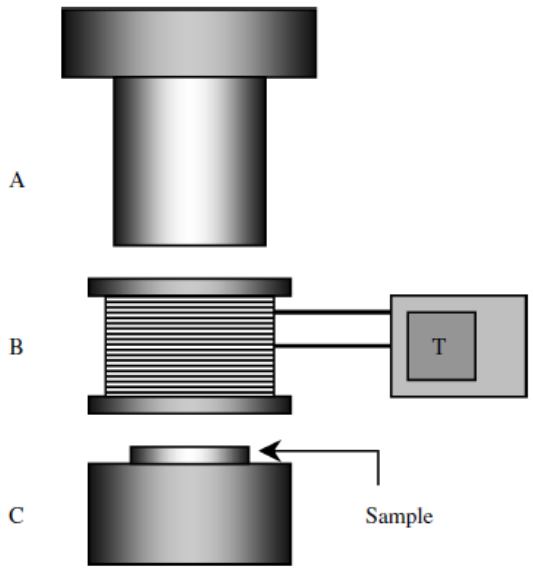


Fig 2.1Illustration of hot press equipment: (A) weighing cylinder, (B) heater, (C) base, (T) temperature controller

In the present study we have used solution cast technique to prepare Polyethylene oxide based polymer electrolytes, because it is one of the easier method for preparation of polymer electrolyte.

2.2PROCEDURE

Preparation of polymer electrolyte based on PEO:

I. Appropriate ratio of polymer host (PEO) was taken and dissolved it in 20 ml Acetonitrile.
II. After swelling of polymer in the Acetonitrile, appropriate amount of salt was added in the solution.
III. Then the solution was stirred for 10 hour.
IV. The obtained solution was then casted on petridishes and allowed to evaporate slowly at room temperature followed by vacuum drying.
V. Thin films of polymer electrolyte were obtained.

FLOW CHART:

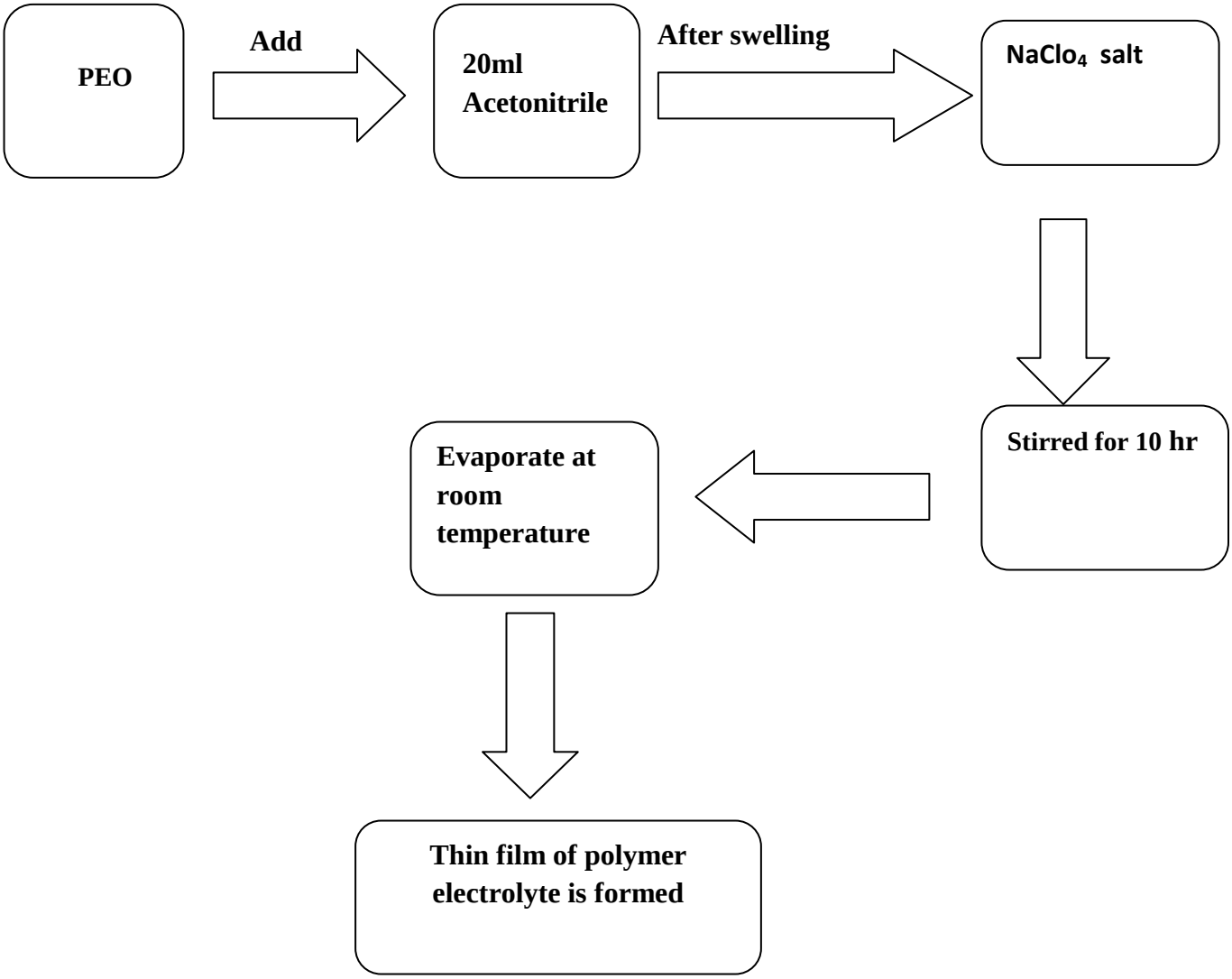


Fig. 2.2 flow chart for sample preparation from PEO

Preparation of polymer electrolyte based on PU :-

The procedure is same as that of preparation of PEO based electrolyte, only Acetonitrile was replaced by Tetrahydrofuran (THF) because PU was not dissolved in the Acetonitrile. The flow chart diagram is given below.

FLOW CHART:-

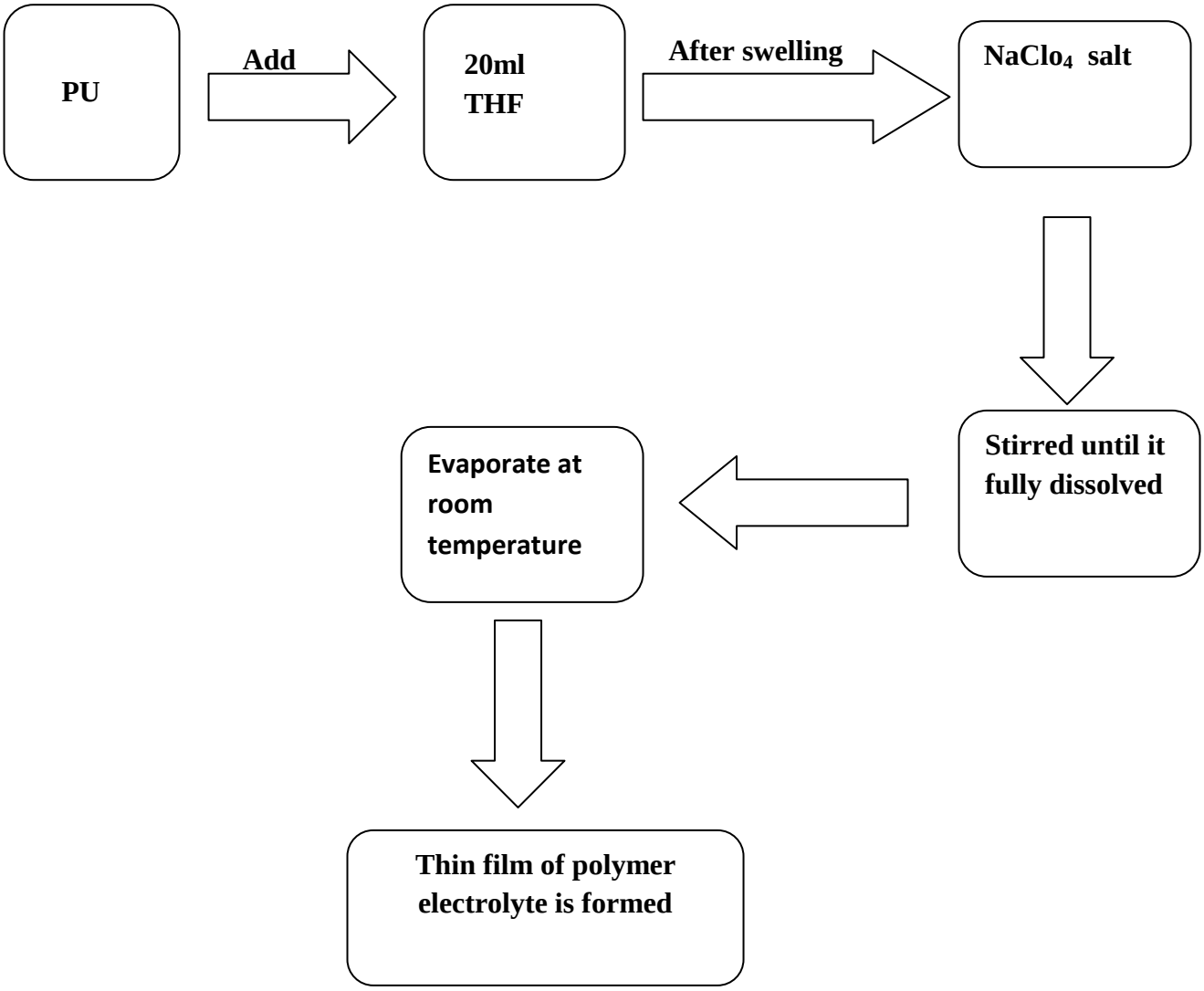


Fig.2.3 flow chart for sample preparation from PU

2.3 CHARACTERIZATION:

Materials properties like structure, surface morphology, thermal, electrical, mechanical, optical etc. should be studied in details in order to understand the chemistry and physics of materials. These experimental characterization techniques also provide useful guideline on the suitability of the material for possible device applications. In the present case we have studied the structural, vibrational, microstructural and electrical properties of the material using X-ray diffraction, FTIR, Scanning electron microscopy and complex impedance analysis respectively.

X-Ray Diffraction: The X-ray diffraction technique is used to determine the atomic arrangements (i. e., crystal structure) of the materials because the inter-planar spacing (d-spacing) of the diffracting planes is of the same order of X-ray wavelength. For a crystal of given d-spacing and wavelength λ, the various orders of reflection occurs only at the precise values of angle θ which satisfies the Bragg condition, i.e. $2d \sin\theta = n\lambda$. The accurate determination of inter-planar spacing, lattice parameters etc. provides an important basis in understanding the various physical properties of the materials. For structural characterization of the polymer, the XRD patterns of all the compounds have been recorded at room temperature (25^0C) using X-ray powder diffractometer (Philips X-ray diffractometer) with Cu kα radiation (λ = 1.5405 Å) in a wide 2θ (Bragg angle) range ($10 \leq 2\theta \leq 60$) at a scanning rate of 3^0/min.

Scanning Electron Microscopy: The surface morphology of different polymers can be observed by microscopy. The surface morphology/micro structural studies of the material sample have been carried out using a computer-controlled scanning electron microscope (SEM) (JEOL T-330). The polymers were platinum coated prior to being scanned under high-resolution field emission gun scanning electron microscope.

Infrared spectroscopy: The chemical aspect, chain structure and physical aspects (i.e., chain orientation, crystallinity, and chain conformation or chain dynamics) can be studied using types of spectroscopic methods. Fourier transform infrared (FTIR) spectra of the electrolytes were recorded with a FTIR spectrometer (Thermo Nicolet Corporation, NEXUS –870) from 4000 to 400 cm^{-1} with a resolution of 2 cm^{-1}.

Impedance Analysis: Complex Impedance Analysis is a powerful technique to characterize the electrical properties of the electrolytes. The complex impedance measurement were carried out using a computer-controlled impedance analyzer (PSM 1735 Impedance Analysis Package (Newton 4^{th} Ltd.)) in the frequency range of 100 mHz to 1MHz at a a.c. signal level of 100 mV at room temperatures. The polymer electrolye film is sandwiched between two stainless steel blocking electrodes for using as cell for the electrical measurement. The complex impedance spectrum data was used to evaluate the bulk D.C. conductivity and other related electrical properties.

CHAPTER-3

3. RESULT AND DISCUSSION

3.1. XRAY DIFFRACTION:

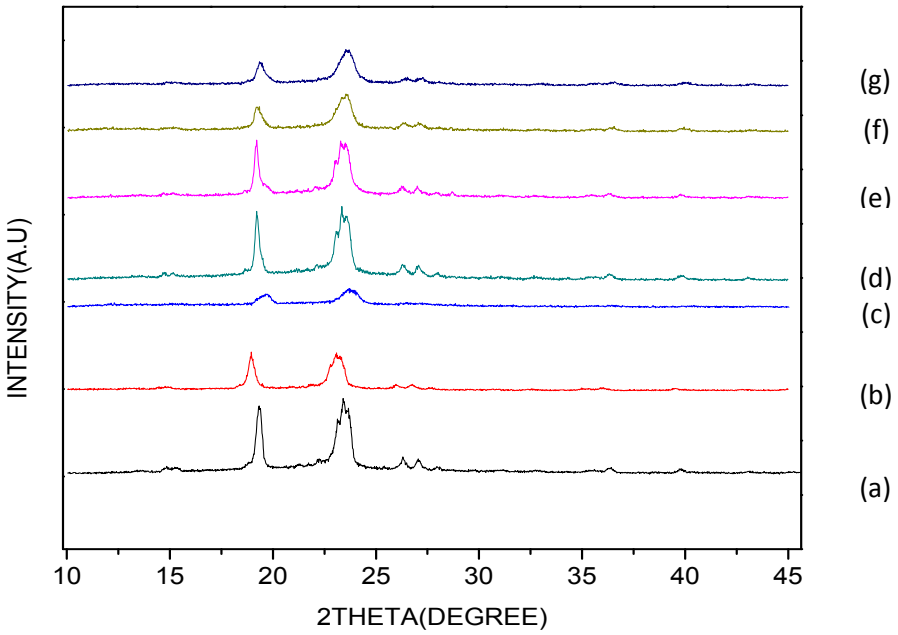


Fig3.1 XRD pattaerns of $(PEO)_x$-$NaClO_4$ (x=09(a),49(b),8(c),20(c),40(d),60(e),80(f),100(g))

The XRD patterns of PEO with different O/Na ratio of polymer electrolytes were depicted in Fig. (3.1). The XRD pattern has a typical feature of several characteristic diffraction peaks attributed to host polymer (i.e. polyethylene oxide (PEO)). The appearance of PEO peaks at ~ 19^0 and 23^0 also agrees well with the literature. The polymer-slat complexes have similar XRD pattern to that of the host PEO indicating the complexation of polymer with salt. No extra peaks are observed in the XRD patterns of complexes indicating that salt is not precipitated. The XRD patterns indicate that the solid polymeric films are composed of a combination of crystalline and amorphous phases.

Determination of crystallite size: Average crystallite sizes can be estimated from the full width half – maxima (FWHM) of the strongest diffraction peak using Scherer's formula.

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

Where, D is the crystallite size, λ is the wave length of Cu k_α (λ = 1.5405 Å), β is the FWHM and Θ is the diffraction angle of the strongest characteristic peak. The inter planer spacing of the strongest peak was found using the Bragg's formula 2d sinθ = nλ, where d is the inter planer spacing. The crystallite sizes and interplaner spacing of PEO with different O/Na ratio (O/Na=0, 4, 8, 20, 40, 60, 80, 100) are given in the Table- 3.1

PEO concentration	**2θ (in degree)**	Interplanar Spacing (A^0)	Crystallite Size (nm)
PEO	19.33	4.587	25.3
	23.44	3.791	10.8
PEO_4-$NaClO_4$	19.33	4.587	23.8
	23.47	3.786	8.1
PEO_8-$NaClO_4$	19.52	4.530	25.1
	23.57	3.771	14.1
PEO_{20}-$NaClO_4$	19.60	4.250	9.5
	23.69	3.723	8.9
PEO_{40}-$NaClO_4$	19.23	4.601	33.4
	23.41	3.717	11.1
PEO_{60}-$NaClO_4$	19.21	4.660	36.3
	23.427	3.793	10.8
PEO_{80}-$NaClO_4$	19.28	4.602	21.1
	23.47	3.787	12.3
PEO_{10}-$NaClO_4$	19.40	4.599	20.1
	23.58	3.787	10.1

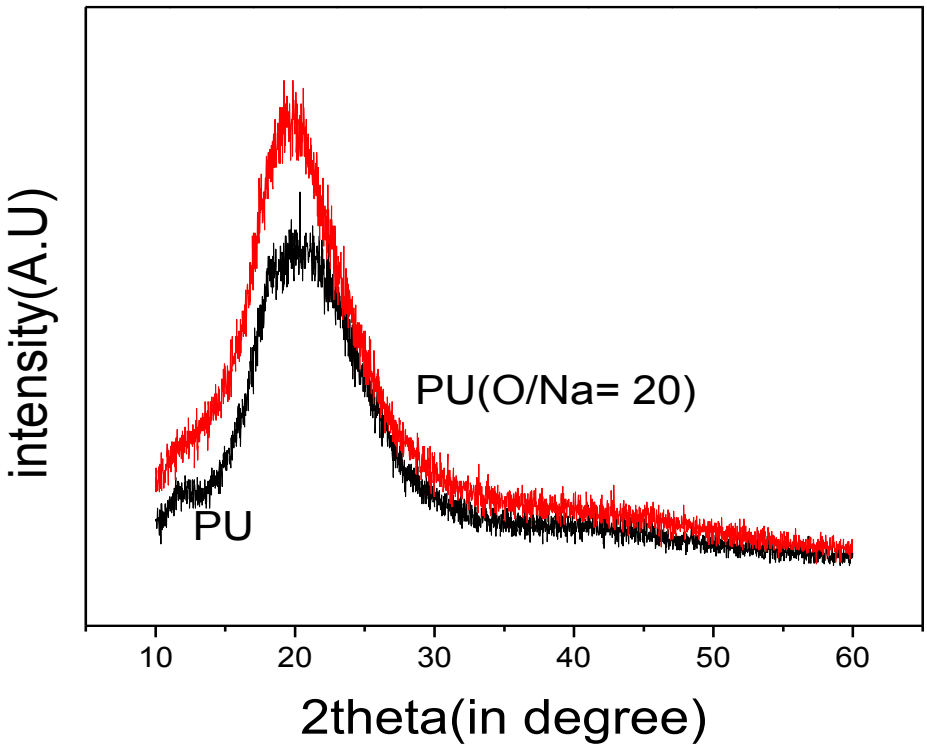


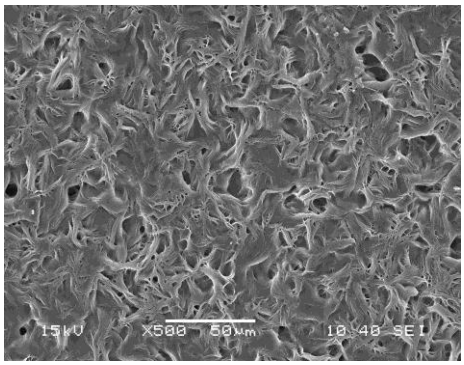
Fig 3.2 XRD pattern of PU and PU_{20}- $NaClO_4$ (O/Na=20)

The XRD patterns of PU and **PU_{20}**- $NaClO_4$ (O/Na=20) are shown in the Figure 3.2. A single main peak is observed in both the cases. In PU the peak appear at 19.978^0 and in PU (O/Na=20) the peak slightly shifted and appear at 20.24^0. The appearance of single peak shows the formation of polymer salt complex. The values of inter-planer spacing of PU (O/Na=0, 20) is given in the Table 3.2.

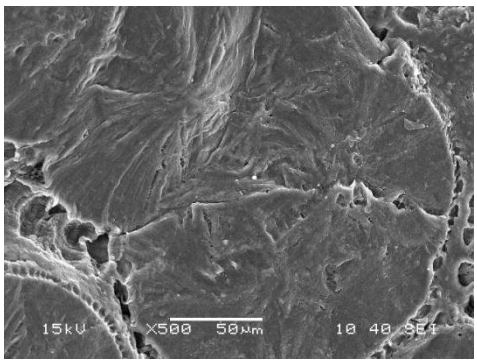
TABLE 3.2:

PU concentration	2θ (in degree)	Interplanar Spacing (A^0)
PU	19.978	4.343
PU_{20}- $NaClO_4$	20.243	4.440

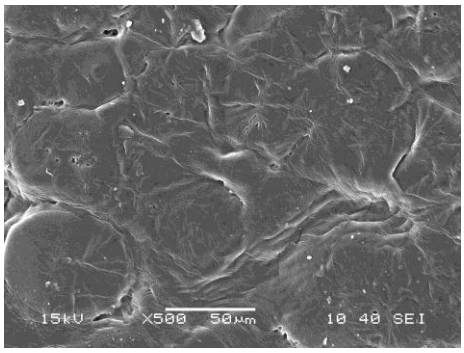
3.2 SCANNING ELECTRON MICROSCOPE ANALYSIS:



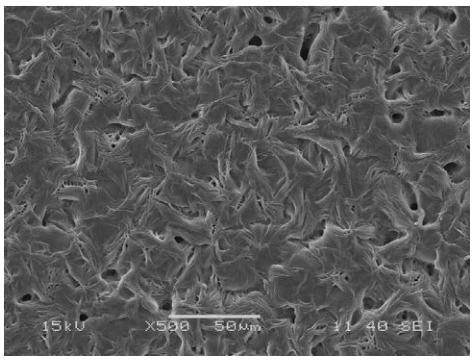
(Fig 3.3-PEO)



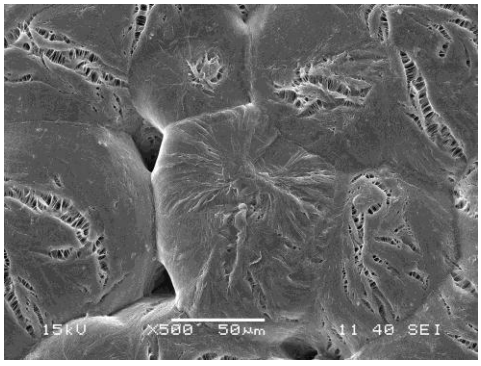
(Fig3.4-PEO (O/Na=4)



(Fig3.5PEO (O/Na=20))



(Fig3.6-PEO (O/Na=40)



(Fig3.7-PEO (O/Na=80))

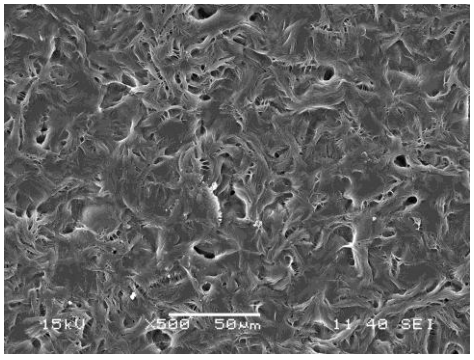


FIG3.8-PEO (O/Na=100))

In Figure 3.3 – 3.8 we have shown the Scanning electron micrographs (SEM) of PEO and polymer-salt complex with different O/Na ratio (O/Na=0, 4, 8, 20, 40, 60,100). The micrographs of the polymer-salt complexes, indicates the presence of distinct spherulites having characteristic lamellar microstructure. The region between spherulite boundaries comprises of amorphous

phase. The micrographs tell that the polymer electrolytes are crystalline in nature with amorphous boundary. There is no systematic change in the surface morphology with different polymer to salt ratio.

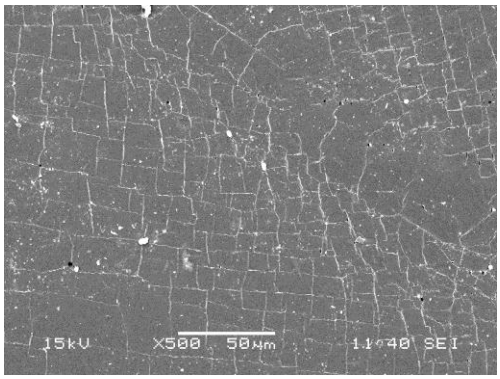


Fig 3.9 (PU)

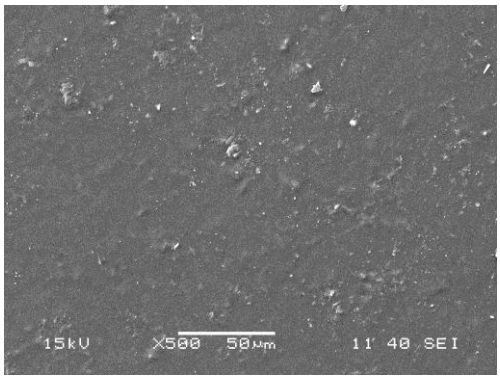


Fig. 3.10 (PU-O/Na-20)

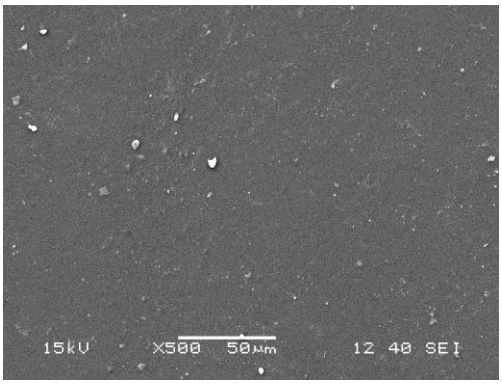


Fig 3.11 PU (O/Na-80)

The Scanning electron micrographs (SEM) of PU and **PU_{20}**- $NaClO_4$ (O/Na=20) are shown in the Figure 3.9- 3.11. From the figures it has been observed the surface morphology become smoother as compared to PU when salt is being added in the PU.

3.3 INFRARED SPECTROSCOPY STUDY:

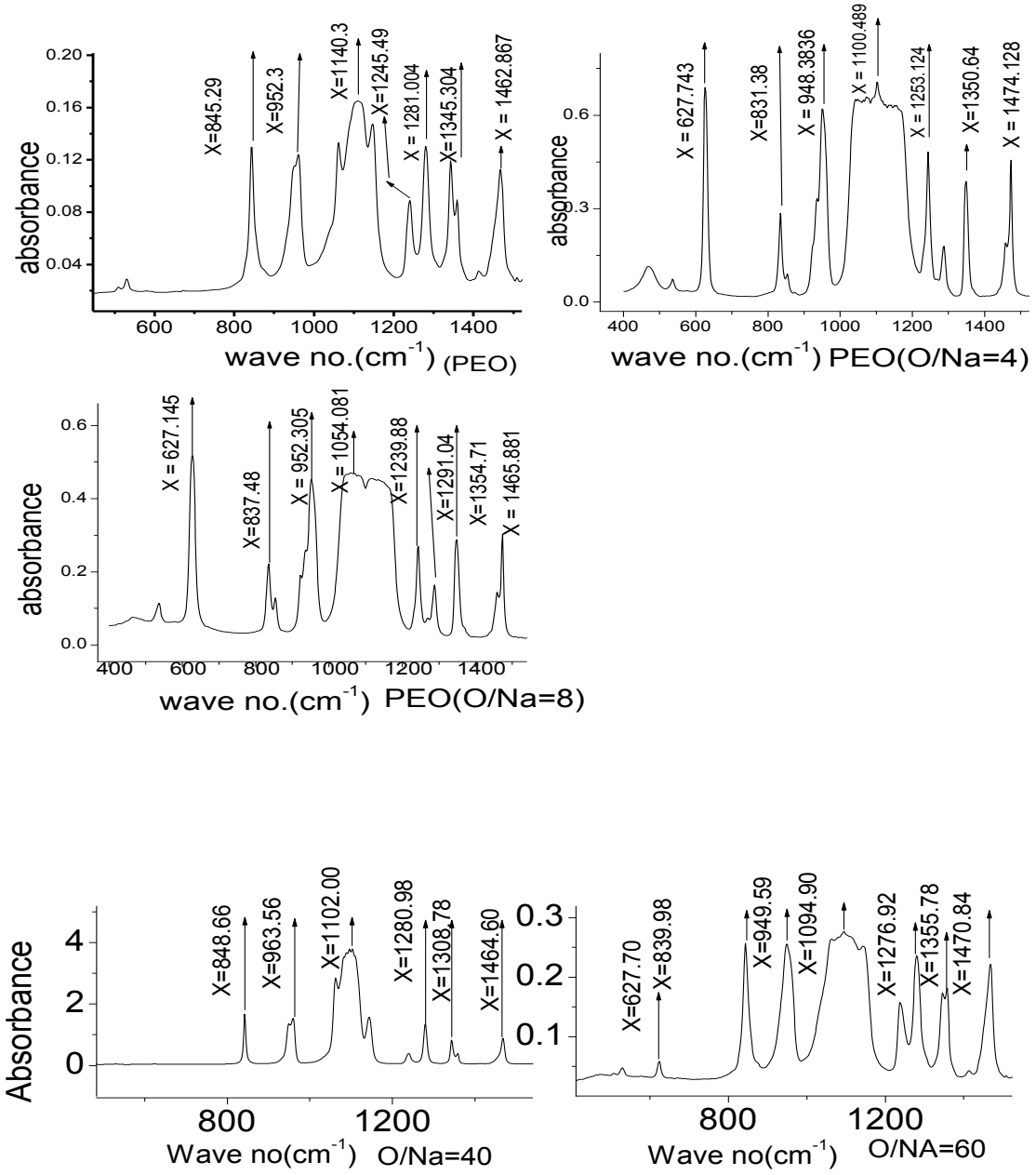


Fig 3.12: IR spectra of PEOx-NaclO_4 for (x=O/Na= 0, 4, 8, 40, 60) in the range 400 to 1500 cm^{-1}

In Figure 3.12 we have shown the IR spectra of PEO and PEOx-NaclO4 for x= 0, 4, 8, 40, 60 in the wave number range 400-1500 cm-1. All the peaks are assigned and shown in the Table.3.3 PEO exhibits characteristic bands in the regions 800-1000 cm-1 corresponds to rocking modes (i.e., r(CH2)), broad band 1000-1200 cm-1 corresponds to stretching mode (i.e., ν(C-O-C)), 1200-1300 cm-1 corresponds to twisting mode; t(CH2) and band around 1350cm-1 and 1456cm-1 corresponds to wagging mode (i.e., w(CH2)) and bending mode (i.e., δ(CH2)) respectively. But in case of polymer salt complex apart from this bands one another band appears around 630cm-1 corresponds to stretching mode of perchlorate band (i.e., ν4(ClO_4^-)). After additions of salt in polymer, the ν(C-O-C) mode become broader as compared to the band of pure PEO indicting the complexation of polymer with salt. There are significant changes in the peak position, peak intensity and FWHM of the peaks of the polymer electrolyte when salts are being added in the polymer.

Table 3.3

Assignment	Appearance In materials	O/Na=0	O/Na=4	O/Na=8	O/Na=40	O/Na=60
ν(ClO_4)	Salt	_	627.743	627.145	_	627.743
r(CH_2)a	PEO	845.29	831.38	837.48	848.66	839.98
r(CH_2)$_S$	PEO	952.3	948.383	952.305	963.56	949.59
ν(COC)	Hybrid	1140.3	1100.489	1054.081	1102	1094.90
t(CH_2)a	PEO	1245.49	1253.124	1239.88	1280.98	1276.92
t(CH_2)s	PEO	1281.004	1291.813	1291.04	_	_
W(CH_2)s	PEO	1345.304	1343.751	1354.71	1308.78	1355.78
δ(CH_2)s	PEO	1462.967	1474.128	1465.881	1464.60	1470.84

STUDY OF ELECTRICAL PROPERTY:

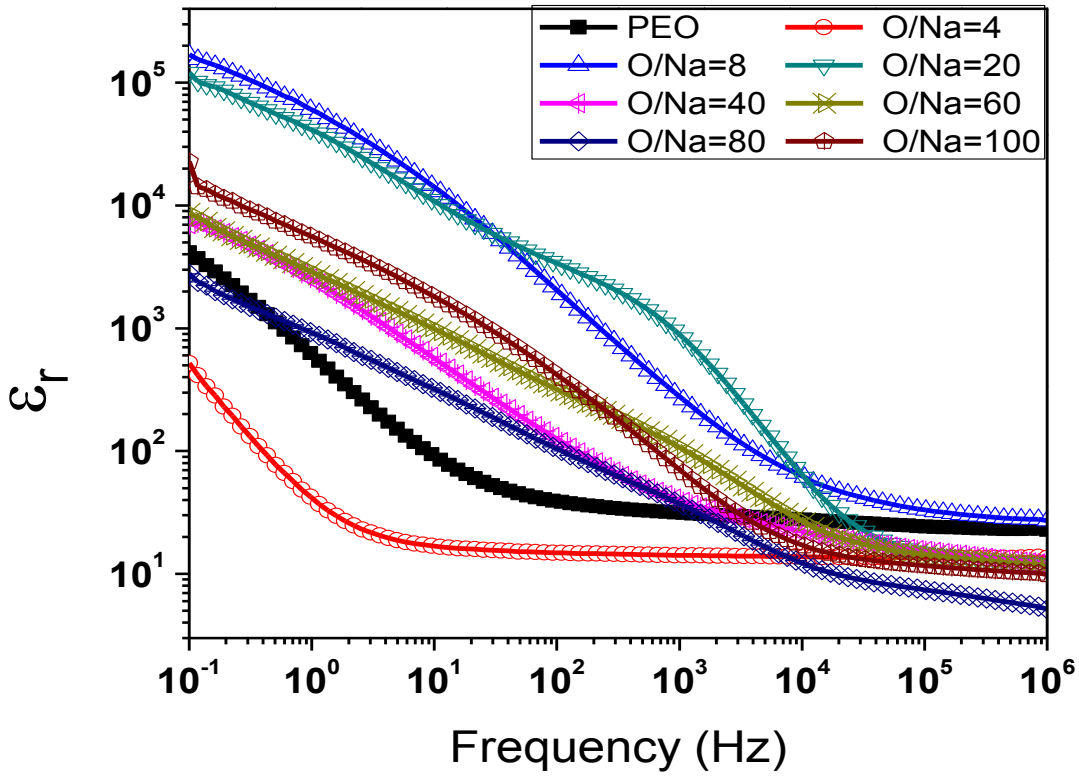


Fig 3.13 Variation of relative dielectric constant with Frequency

Complex impedance spectroscopy is a powerful technique to study relaxation phenomena in the material and also to calculate the D.C. electrical conductivity of the materials. Figure 3.13 shows the variation of relative dielectric constant with frequency for different polymer to salt ratio of PEO based polymer electrolytes. For all the cases the relative dielectric constant decreases sharply in the lower frequency region and showing a frequency independent value at higher frequency regions irrespective of polymer to salt ratio. The decrease of ε_r with increase in frequency may be attributed to the electrical relaxation processes.

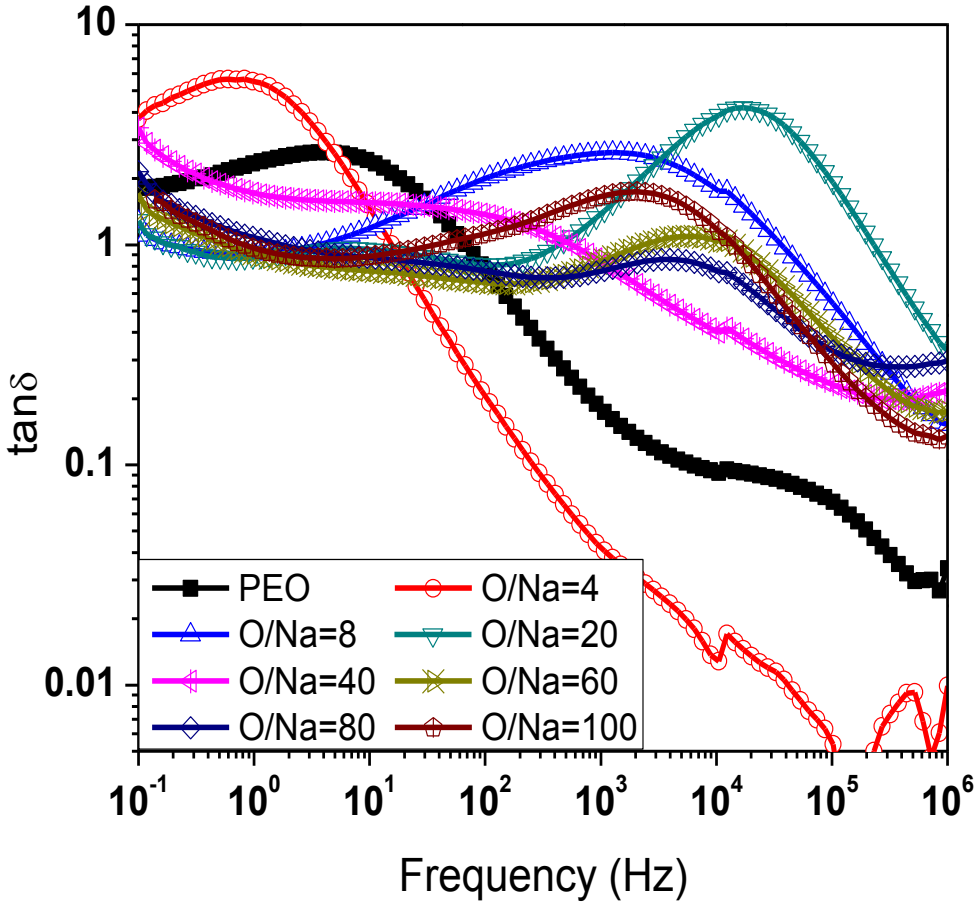


Fig 3.14 Variation of dielectric loss with Frequency

Figure 3.14 shows the variation of tangent loss with frequency for different polymer to salt ratio of polymer electrolyte. The tangent loss spectra of all these samples are characterized by peaks appearing at characteristic frequencies. The appearance of peaks for each concentration in the loss spectrum (tangent loss) suggests the presence of relaxing dipoles in the polymer electrolyte.

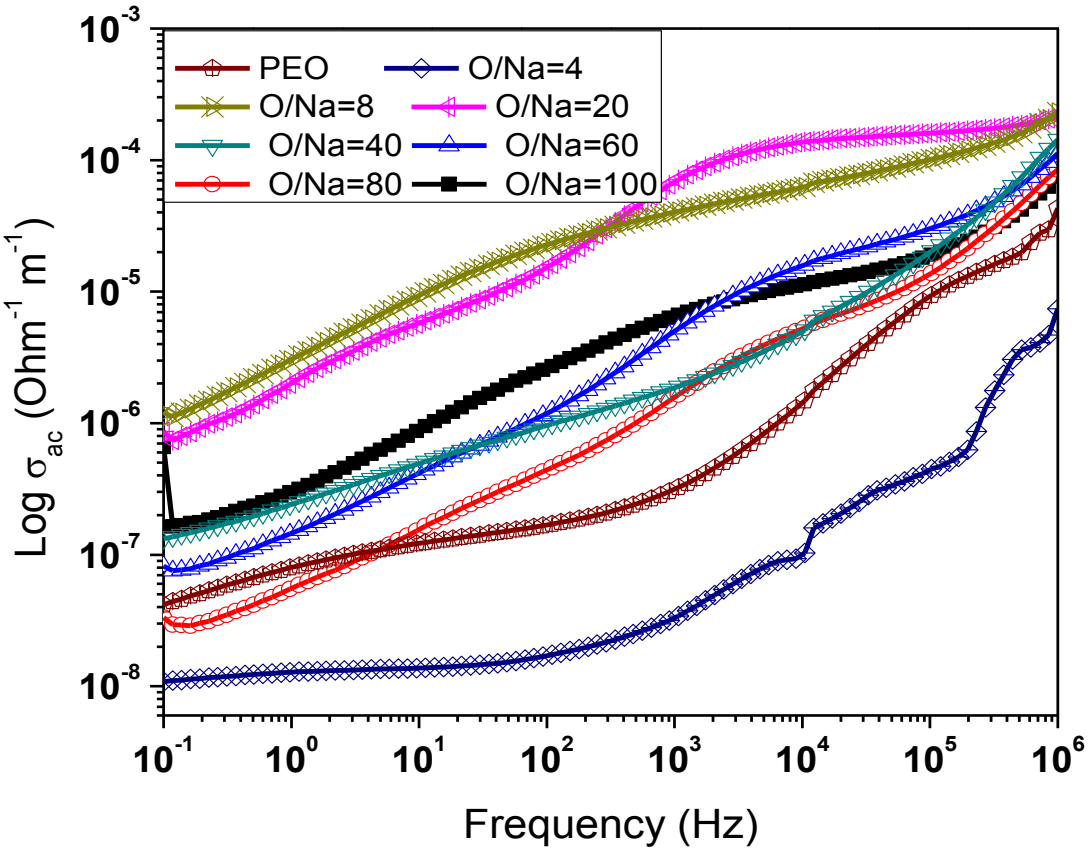


Fig 3.15 Variation of a. c. conductivity with Frequency

The frequency dependence of AC conductivity for different concentration is shown in Fig 3.15. The AC conductivity (σ_{ac}) of the material was calculated using measured dielectric by the relation: $\sigma_{ac}=\omega\epsilon_r\epsilon_0 \tan\delta$, where ($\omega=2\pi f$) is the angular frequency, ϵ_0 the permittivity of the free space. The AC conductivity pattern indicates a progressive rise in a.c. conductivity with increase infrequency.

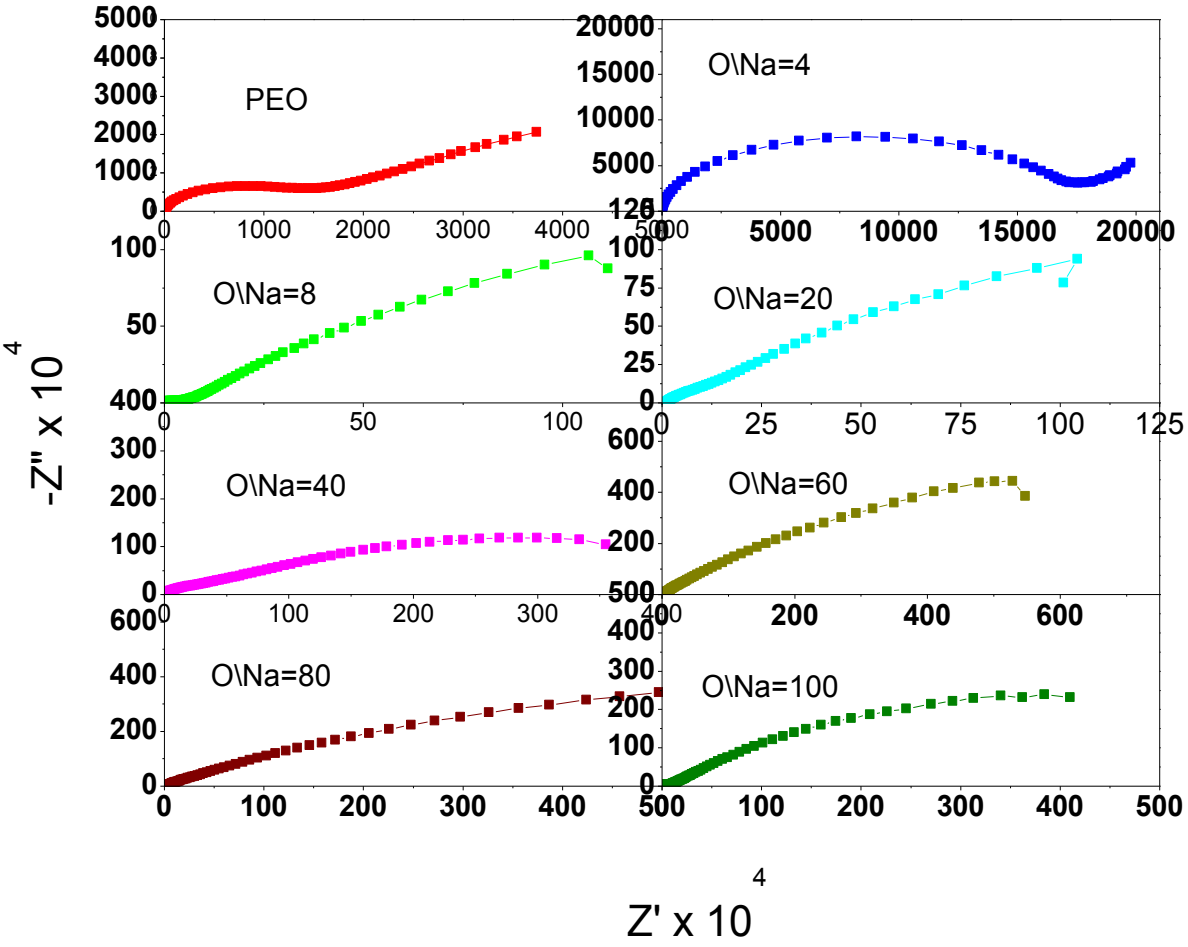


Fig 3.16 Complex impedance spectrum of PEO_x-$NaClO_4$.

Figure 3.16 shows the complex impedance spectrum of PEO_x-$NaClO_4$ with different values of x (i.e., x=0, 4, 8, 20, 40, 60, 80,100). The typical complex impedance spectra (i.e., Nyquist plot) of the samples comprises of a broadened semicircle in the high frequency region followed by a tail (spike) in the lower frequency region for low polymer to salt ratio. But for higher polymer-salt ratio, only one incomplete semicircles have been observed. The high frequency semicircle is due to the bulk properties whereas the low frequency spike arises due to the material-electrode interface of the material. The intercept of the semicircle with the real axis (Z') gives rise to the bulk (ionic) resistance (R_b) of the materials.

The d. c. electrical conductivity (σ_{dc}) of the material was evaluated from the complex impedance spectrum using the relation $\sigma = (1/R_b)^* (t/a)$ where t is the thickness and a is the area of the sample.

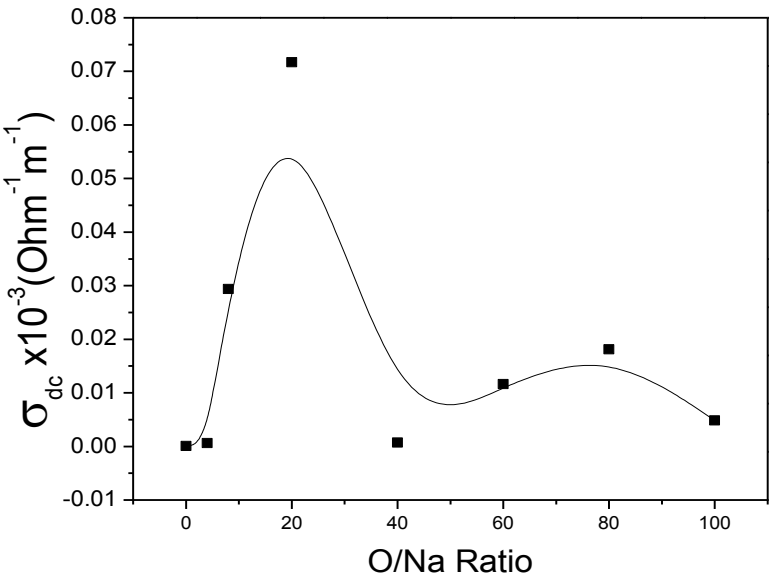


Fig. 3.17 Variation of d. c. conductivity (σ_{dc}) with different value of x PEO_x-$NaClO_4$

Fig. 3.17 Variation of d. c. conductivity (σ_{dc}) with different value of x for PEO_x-$NaClO_4$ (i.e., x=0, 4, 8, 20, 40, 60, 80, 100). From the graph it has been observed that the D.C. electrical conductivity increases with increase in polymer to slat ratio and attains a maximum value for x = 20. On and above x = 20 the conducvity decreases. In the present study, the maximum conductivity was found for O/Na ratio 20.

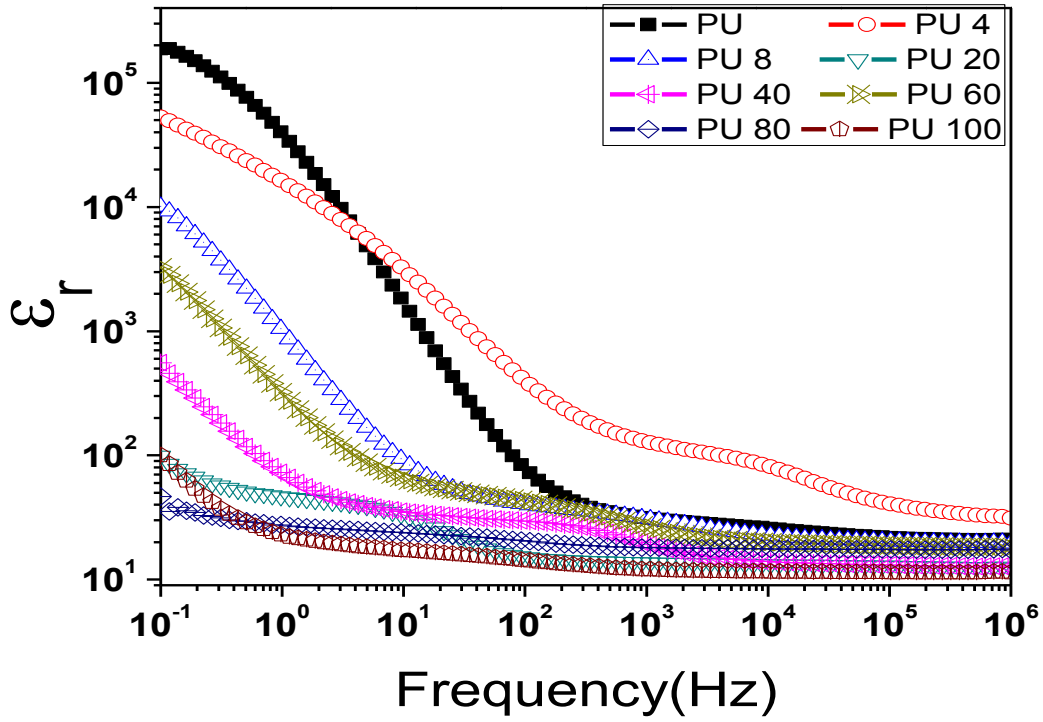


Fig 3.18 Variation of relative dielectric constant with frequency for PU_x-$NaClO_4$.

Fig 3.18 shows the variation of dielectric constant with frequency of PU_x-$NaClO_4$ for different value of x. Like PEO based polymer electrolyte, the dielectric constant decreases with increase in frequency. There is strong frequency dispersion of permittivity is observed in the low frequency region followed by a nearly frequency independent behavior at higher frequency regions.

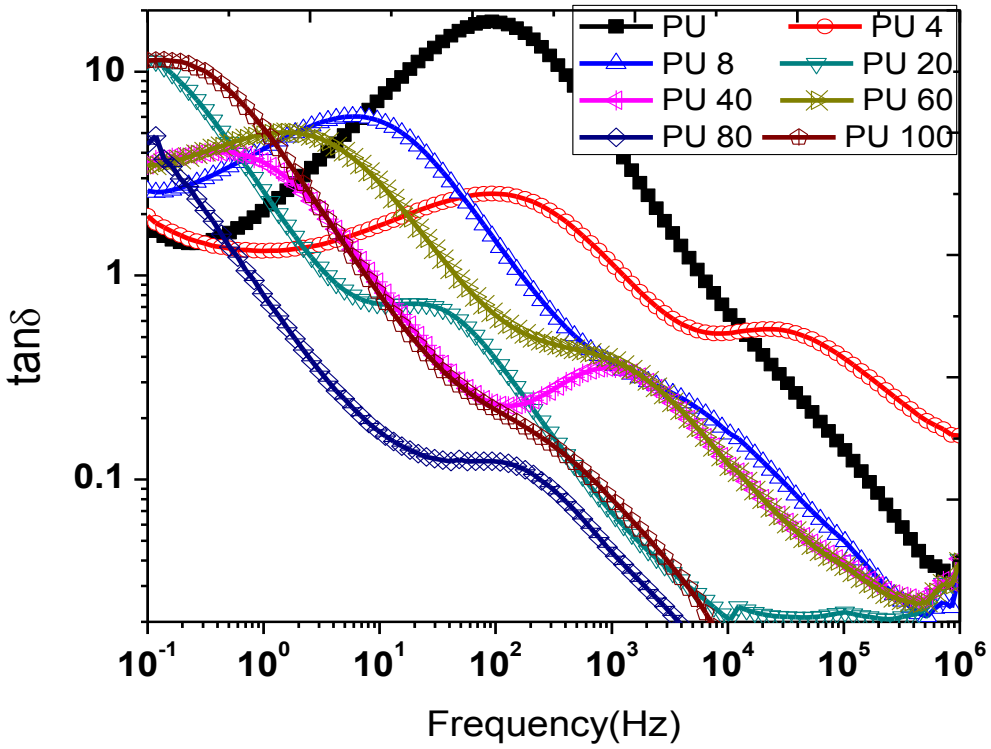


Fig 3.19 Variation of dielectric loss with Frequency

Fig 3.19 the variation of tan δ with frequency at different O/Na ratio (O/Na=0, 4, 8, 20, 60, 80,100) for PU_x-$NaClO_4$ electrolyte. The variation provides tan δ with frequency showed a peak for pure polymer. But in case of polymer slat complexes, two peaks are observed in the dielectric loss vs. frequency spectra. The presence of two peaks related to two different relaxation phenomena.

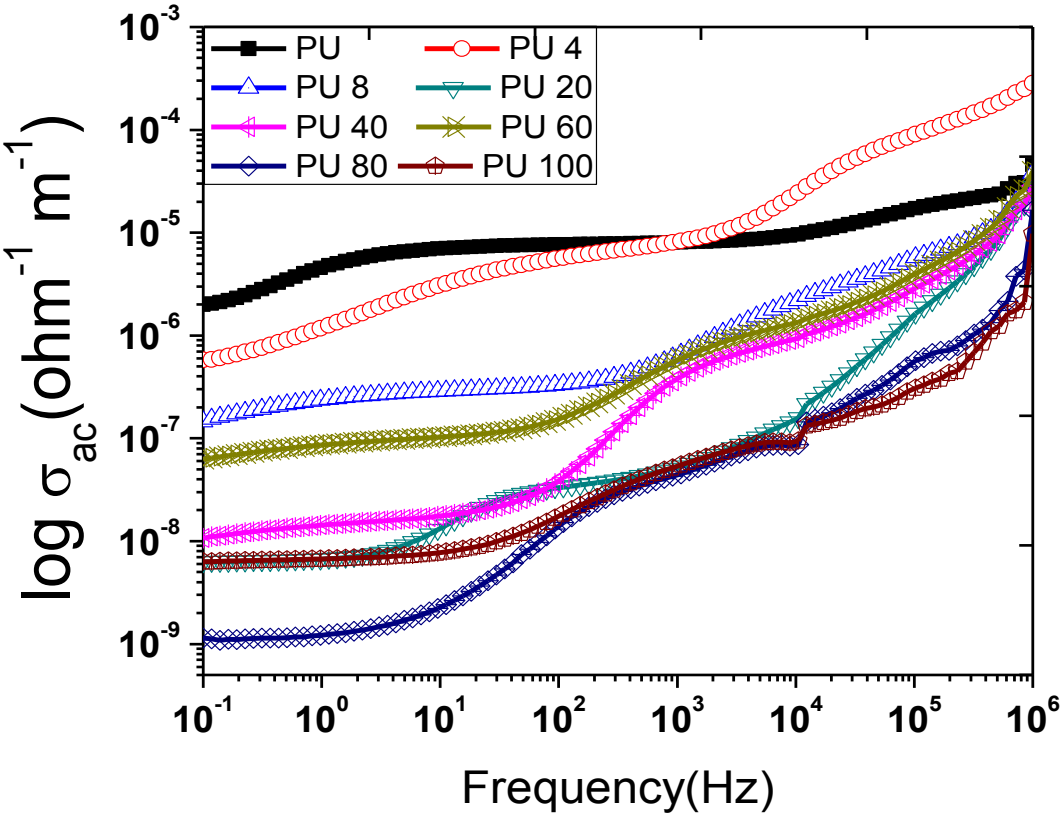


Fig 3.20 Variation of a. c. conductivity with Frequency

The frequency dependence of A.C. conductivity of PU_x-$NaClO_4$ electrolyte for different concentration (i.e., x=O/Na=0, 4, 8, 20, 60, 80,100) is shown in 3.20. The A.C. conductivity (σ_{ac}) of the material is calculated using measured dielectric explained above. The A.C. conductivity pattern indicates a progressive rise in A.C. conductivity on increasing frequency.

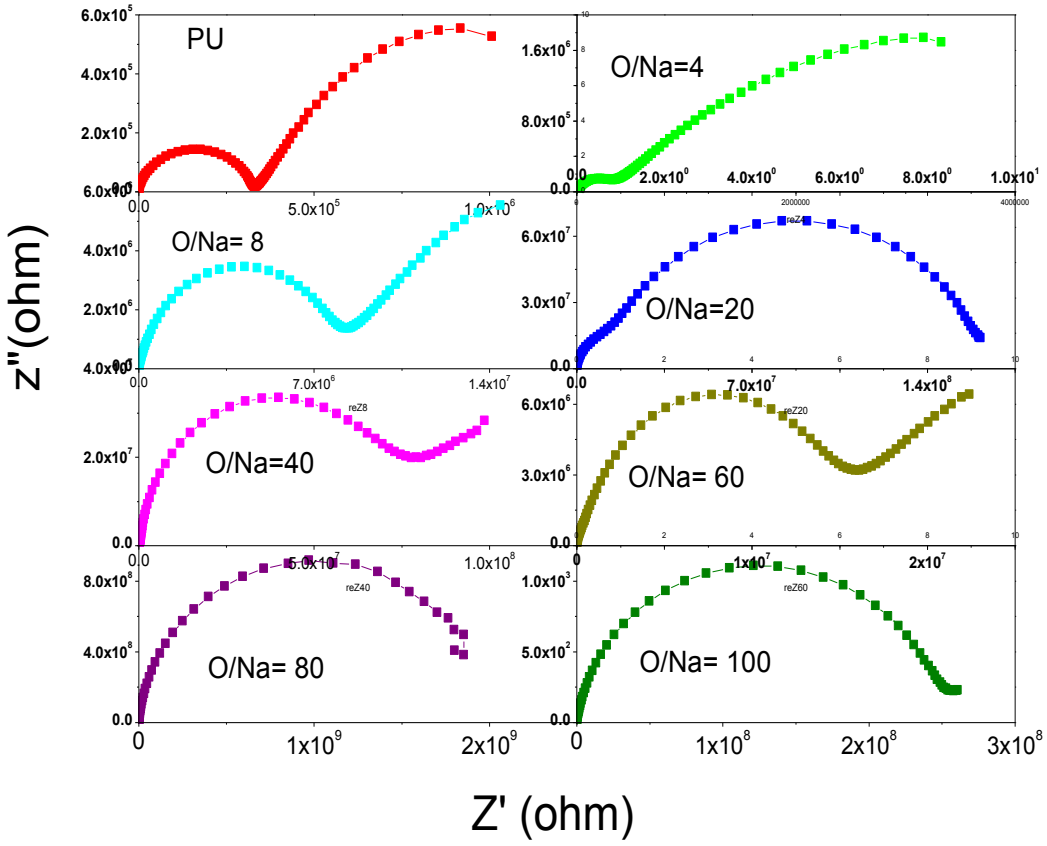


Fig. 3.21 Complex Impedance Spectra

The complex impedance spectra (i. e., Z' vs. Z'') of PU_x-$NaClO_4$ electrolyte at different concentration of O/Na (O/Na=0, 4, 8, 20, 60, 80, 100) are shown in Figure 3.21. For low concentration of polymer to salt ratio two semicircular arcs have been observed, where as for higher concentration of polymer to salt ratio only one semicircular arc have been observed.

CHAPTER-4

CONCLUSION

Two groups of Polymer Electrolytes based on Polyethylene Oxide, (CH2-CH_2-O) and Polyurethane, (RNHCOOR′) as polymer host and $NaClO_4$ as salt were prepared by solution cast technique with different O/Na ratio (O/Na=0, 4, 8, 20, 40, 60, 80, 100). The structural, microstructural/morphological, vibrational and electrical properties of the polymer electrolyte have been studied with different experimental techniques. We have drawn the following conclusions

I. The complexation of the polymer electrolyte has been studied using XRD analysis. The crystallite size (using Scherer's formula) and inter planner spacing of the polymer electrolytes were calculated from the XRD data

II. The polymer salt complexation again confirmed by Infrared Spectroscopy (IR).

III. The microstructure/surface morphology of the Polymer Electrolytes was analyzed by Scanning electron microscope. . The SEM micrographs showed the existence of both crystalline and amorphous phases.

IV. Frequency dependence of dielectric properties and A.C. electrical conductivity of polymer electrolytes were studied at different the frequency range (100 mHz to 1MHz). Conductivity of the polymer electrolytes have been calculated from the complex impedance spectra.

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